Supporting Information

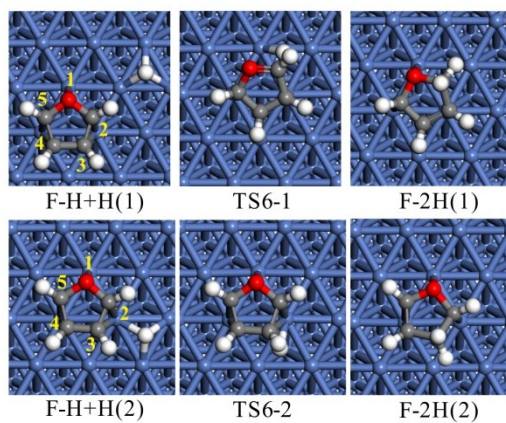## A Theoretical Insight into Furfural Conversion Catalyzed on Ni(111) Surface

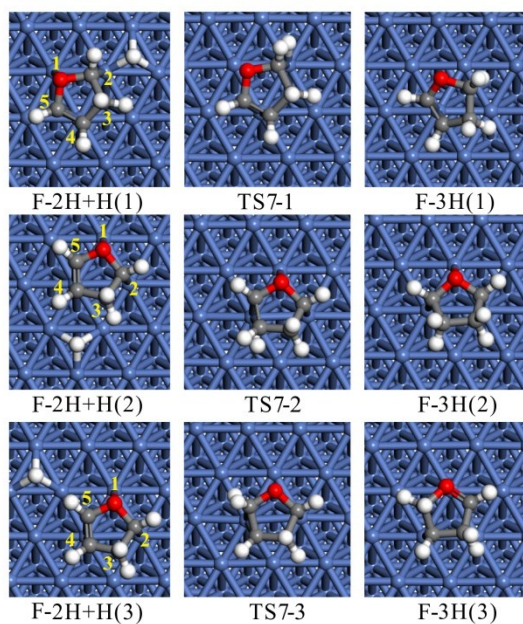Guoqing Ren, [a,#]   Guiru Wang,[b,c,#]   Hua Mei,[a,*]   Yan Xu,[a,*]   Ling Huang [b,*]

Tetrahydrofuran formation *via* hydrogenation of furan

Actually in furan, there are two kinds of hydrogenation ways: one is the H atom addition onto C2 or C5, which are defined as α-carbon; the other is the H atom addition onto C3 or C4, which are defined as β-carbon. As a consequence, the activation barriers of the first-step hydrogenation on C2 (α-carbon) and C3 (β-carbon) were respectively 94.5 and 81.9 kJ/mol, and the corresponding reaction energies are endothermic by 38.0 and 35.0 kJ/mol, respectively. As shown in **Figure S1**, the results indicate that the first-step hydrogenation of furan *via* H atom onto C3 (β-carbon, *via* TS6-2) is more kinetically and thermodynamically favorable than that onto C2 (α-carbon, *via* TS6-1). Furthermore, once the F-2H intermediate (TS6-2) forms, subsequently there are three possible hydrogenation ways: the first one is H atom addition onto C2 atom (TS7-1), the second one is H atom addition onto C4 atom (TS7-2), and the third one is the H atom addition onto C5 atom (TS7-3), for which the corresponding activation barriers are 63.4, 56.4, and 96.5 kJ/mol, and the reaction energies are 28.5, -10.8 and 52.0 kJ/mol, respectively. The results indicate that the hydrogenation of F-2H by adding an H atom onto C4 (TS7-2) is the most preferred in both kinetics and thermodynamics. Moreover, the successive hydrogenation of F-3H (2) will lead to the tetrahydrofuran, and the related activation barriers are 63.0 kJ/mol (F-3H+H→F-4H, *via* TS8) and 77.1 kJ/mol (F-4H+H→F-5H, *via* TS9), with the reaction energies of -35.9 and -9.6 kJ/mol, respectively.
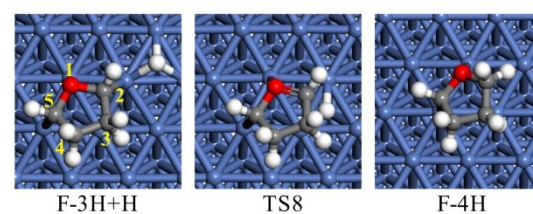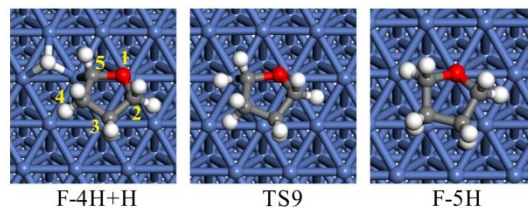
F-2H formation

F-H+H(1)   TS6-1   F-2H(1)

F-H+H(2)   TS6-2   F-2H(2)

F-3H formation

F-2H+H(1)   TS7-1   F-3H(1)

F-2H+H(2)   TS7-2   F-3H(2)

F-2H+H(3)   TS7-3   F-3H(3)

F-4H formation

F-3H+H   TS8   F-4H

F-5H formation

F-4H+H   TS9   F-5H

Figure S1.   The structures of the initial states, transition states, and final states for the hydrogenation reactions of furan. The number 1-7 are used to label the different atoms in reaction species.